Available online at www.sciencedirect.com

ScienceDirect

Acta Materialia 56 (2008) 3711–3722

Acta MATERIALIA

www.elsevier.com/locate/actamat

Temperature memory effect in Cu–Al–Ni shape memory alloys studied by adiabatic calorimetry

Javier Rodríguez-Aseguinolaza [b], Isabel Ruiz-Larrea [a,*], Maria Luisa Nó [a], Angel López-Echarri [b], José María San Juan [a]

[a] Departamento Fisica Aplicada II, Universidad del País Vasco, Bilbao, Vizcaya, Spain
[b] Departamento de Física Condensada, Universidad del País Vasco, Bilbao, Vizcaya, Spain

Received 14 January 2008; received in revised form 4 April 2008; accepted 4 April 2008

Abstract

The temperature memory effect exhibited by Cu–Al–Ni shape memory alloys was studied by means of adiabatic calorimetry and microscopic observations. The harmonic, anharmonic and electronic contributions to the lattice specific heat were estimated by using the experimental data of the metallic components. The obtained results provide an accurate baseline for the quantitative study of the martensitic phase transformations as a function of the thermal history in these alloys. The specific heat of a Cu–Al–Ni sample was measured from 140 to 350 K throughout the phase transition region, and the temperature memory effect was carefully studied. These results are in good agreement with the optical observations as a function of temperature. The global behaviour of the martensitic transformation as regards the temperature memory effect is discussed and interpreted in terms of the microscopic mechanisms of nucleation and motion of the martensite plates.

Keywords: Shape memory alloys; Adiabatic calorimetry; Martensitic transformation; Cu–Al–Ni; Optical microscopy

1. Introduction

Shape memory alloys (SMAs) exhibit a reversible and diffusionless thermoelastic martensitic transformation that is responsible for their specific thermomechanical properties, such as superelasticity and shape memory [1]. Because of these properties, SMAs are considered to be smart materials and are widely used as sensors and actuators in different kinds of technological applications [2–6]. However, during most real applications the working service conditions fluctuate and do not guarantee complete martensitic transformation. If only partial transformation takes place, an unexpected kinetic behaviour, scarcely studied in the literature, is observed. In particular, a new memory effect was first reported in Ti–Ni [7–9], as well as in other shape memory alloys such as Cu–Al–Ni [10], by differential scanning calorimetry (DSC). The so-called temperature memory effect (TME) appears when a martensitic–austenitic transformation is incomplete. This partial cycle is made by heating the sample to an intermediate arrested temperature (T_a) between the austenite start (A_s) and finish (A_f) temperatures, and then cooling down to below the martensite finish temperature (M_f). It is shown that the following complete heating cycle presents an additional DSC peak, closely related to T_a.

The aim of this work was to study the TME in a Cu–Al–Ni single crystal by using adiabatic calorimetry and optical microscopy. The sample composition was: Cu (82.3%) Al (13.7%) Ni (4%) (wt.%), which is referred to as CAN4, after the notation in Ref. [11]. The experimental resolution attained by this calorimetric technique makes it useful for the investigation of the TME and its influence upon the specific heat around the martensitic transformation. In

---

[*] Corresponding author. Tel.: +34 946015324; fax: +34 946013500.
E-mail address: isabel.ruiz@ehu.es (I. Ruiz-Larrea).

1359-6454/$34.00 © 2008 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.actamat.2008.04.010

addition, direct microscopic observation of the phase transition by means of in situ optical microscopy has been carried out. The combination of both results could clarify the physical mechanisms present in the TME. In addition, previous DSC and dilatometric measurements were performed.

The phase transformation specific heat results corresponding to various Cu–Al–Ni alloys and different thermal histories can only be successfully compared after a suitable deconvolution of the alloy specific heat. Several attempts to establish a reliable specific heat baseline valid for the related Cu–Al–Zn shape memory alloy have been published [12–14]. These studies were accomplished by means of semi-empirical approaches using the Debye and the Einstein models. In our case we tried to estimate the lattice contribution to C_p in Cu–Al–Ni alloys by directly using the phonon spectrum of the metallic components [15–17]. The addition of the anharmonic and electronic contributions would make this model valid for various alloy compositions in order to study the phase transformation thermodynamic functions.

2. Model for the lattice contribution to the specific heat in Cu–Al–Ni alloys

In the absence of any precise knowledge of the lattice phonon frequencies of these alloys, the use of the Debye model by means of an empirical characteristic temperature (θ_D) can be a reasonable approach to describe the lattice contribution to the specific heat. However, this procedure is not usually able to describe its behaviour in wide temperature ranges, due to the simplicity of the phonon frequency distribution: $g(\nu) \propto \nu^2$ for $0 < \nu < \nu_D$, where $\nu_D = k_B\theta_D/h$, k_B is the Boltzmann constant and h is the Planck constant) [18]. In some cases, the specific heat of an alloy can be approximated by the simple addition of its metal components' specific heat [18]. However, for Cu–Al–Ni alloys the direct addition of the experimental specific heat at constant pressure (C_p) of copper [19], aluminium [20,21] and nickel [22] conveniently weighed by the atomic composition in CAN4 shows a higher value (about 3% at 340 K) than the one observed, as seen in Fig. 4a. In principle, this discrepancy is related to changes in the alloy lattice structure as regards their metallic components and could affect the following contributions to C_p: the harmonic specific heat of the alloy faced up to the metal components, the anharmonic specific heat and the electronic contribution. In the present case, the ferro-paramagnetic phase transition in pure nickel at 630 K, which does not occur in the alloy, can also affect this calculation.

2.1. Harmonic specific heat

Unlike chemical reactions, where the bonding rearrangement significantly alters the vibrational spectrum and consequently the lattice specific heat of the solid, the metallic bonding in alloys does not show such noticeable changes from the single metal components. This means that the density of the phonon spectrum of the alloy should be quite similar to those of the metals. In our case, the experimental results show very similar phonon distributions for the three metals involved [15–17], as can be schematically seen in Fig. 1. Using these results, we are able to determine the harmonic specific heat C_h of each metallic component, which in principle can be associated to the specific heat at constant volume C_v. The validity of this approach for a wide temperature range is based on the slight changes with temperature observed in the density of states [15,23], together with the relative independence of C_v from small changes in the frequency spectrum. Within the framework of our model, these changes will be taken into account as anharmonic effects. The frequency range of the density of the vibrational states for each metal is conveniently divided into N equal parts ($\delta\nu_i$) from $\nu = 0$ to $\nu = \nu_{max}$. The contribution to C_h of modes with frequencies between ν_i and $\nu_i + \delta\nu_i$ is calculated by means of a single Einstein function $f_E(\nu_i, T)$ with a ν_i characteristic frequency. The total mode contribution is then:

$$C_h = \sum_{i=1}^{N} g(\nu_i) f_E(\nu_i, T)\delta\nu_i \tag{1}$$

$$f_E(\nu_i, T) = 3nk_B \frac{x^2 e^x}{(e^x - 1)^2} \tag{2}$$

where n is the number of atoms, k_B is the Boltzmann constant, $x = \frac{h\nu_i}{kT}$ and h is the Planck constant.

When the lack of experimental information about the phonon distribution does not permit this procedure, the simpler Debye model can be used as an alternative approximation. For the sake of comparison, the normalized Debye phonon distributions for Cu [24], Al [21] and Ni [22] for $\theta_D = 320$, 405 and 391 K, respectively, are shown in Fig. 1. As can be seen, the use of these Debye distributions undervalues the low frequency modes around the

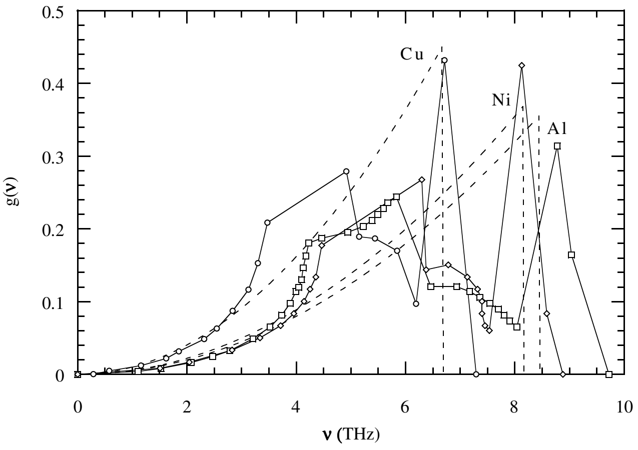

Fig. 1. Normalized vibration spectrum of Cu, Al and Ni: $\int g(\nu)d\nu = 1$. The dotted lines represent the Debye phonon distribution for Debye characteristic temperatures: 320, 405 and 391 K ($\nu_D = 6.67$, 8.44 and 8.15 THz) respectively.